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(11) Publication number : **0 503 856 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number : **92301935.0**

(51) Int. Cl.⁵ : **B41M 5/30**

(22) Date of filing : **06.03.92**

(30) Priority : **11.03.91 JP 44692/91**
06.06.91 JP 134999/91
24.06.91 JP 151702/91

(43) Date of publication of application :
16.09.92 Bulletin 92/38

(84) Designated Contracting States :
DE FR GB

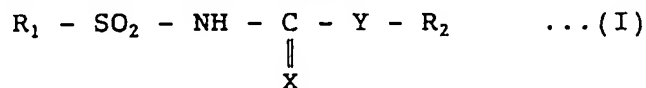
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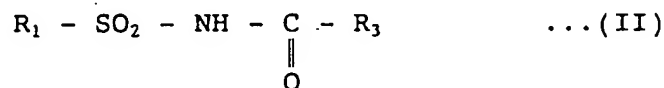
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(54) **Thermosensitive recording material.**

(57) A thermosensitive recording material providing a high storage durability for colored images, and a satisfactory whiteness, comprises a thermosensitive colored image-forming layer formed on a sheet substrate and comprising a colorless dye precursor, and a new color developing agent which comprises an aromatic sulfon(thio)amide compound of the formulae (I) and (II) :



and



wherein X and Y are O or S; R₁ is an unsubstituted aromatic mono- or poly- cyclic group, or a substituted phenyl group having a lower alkyl, aryl or halogen; R₂ is a substituted alkyl group having an aralkyl or aryloxy, unsubstituted aromatic mono- or poly- cyclic group, or a substituted aromatic mono- or poly- cyclic group having an alkyl, alkenyl, aryl, aralkyl, alkyloxy, aryloxy, aralkyloxy, alkylmercapto, arylmercapto, aralkylmercapto, alkyloxycarbonyl, aryloxy-carbonyl, aralkyloxycarbonyl or halogen, and R₃ is a substituted phenyl group with a low alkyl, aryl or halogen, unsubstituted aromatic mono- or poly- cyclic group or aliphatic or cycloaliphatic hydrocarbon group.

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BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a thermosensitive recording material on which colored images are formed by heating. More particularly, the present invention relates to a thermosensitive recording material capable of forming thereon colored images having a high persistency for a record storage thereof for a long time.

The thermosensitive record material is able to record thereon colored images exhibiting an excellent resistance to moisture, heat, oily and fatty substances, and plasticizers, and thus has a superior stability when stored for a long time, and has a high whiteness, and therefore is useful as colored image-recording sheets, sheets for use in facsimiles and cash dispensers, as passenger tickets, commuter's passes, labels such as POS labels, cards such as prepaid cards, and as transit passes.

2. Description of the Related Arts

15 It is known that a conventional thermosensitive recording material comprises a supporting substrate, for example, a paper sheet, synthetic paper sheet, or plastic resin film, and a thermosensitive colored image-forming layer formed on a surface of the supporting substrate and comprising an electron-donative dye precursor, for example, a leuco basic dye, an electron-acceptive color-developing agent consisting of an organic acid substance, for example, a phenol compound, and a binder. When the thermosensitive colored image-forming layer is heated, colored images are recorded thereon by a reaction of the dye precursor with the color-developing agent.

This type of thermosensitive recording material is disclosed in Japanese Examined Patent Publication Nos. 43-4,160, 45-14,039 and 48-27,736, and is widely employed in practice.

25 Namely, the thermosensitive recording material is advantageous in that colored images can be easily formed only by heating, and the recording apparatus can be made relatively compact and small size, at a low cost, and is easily maintained, and thus is useful as an information-recording material for various outputs or printers used with, for example, computers, facsimile machines, automatic ticket-vending machines, scientific measurement recorders, and CRT medical measurement recorders.

30 Nevertheless, the conventional dye-forming type thermosensitive recording materials in which the thermosensitive colored image-forming layer comprises a conventional color-developing agent together with the dye precursor and the binder, is disadvantageous in that the reaction of the dye precursor with the color-developing agent is reversible, and thus the resultant colored images fade with a lapse of time. This fading of the colored images is accelerated by exposure to light, high temperatures and high humidity, and promoted by contact with an oily or fatty substance or a plasticizer, and the colored images fade to an extent such that the faded images cannot be recognized.

Many attempts have been made to inhibit the color-fading of the colored images formed on the conventional thermosensitive colored image-forming layer containing a substantially colorless dye precursor comprising a lactone ring compound.

40 For example, Japanese Unexamined Patent Publication Nos. 60-78,782, 59-167,292, 59-114,096 and 59-93,387 disclose a thermosensitive colored image-forming layer containing a phenolic antioxidant.

Japanese Unexamined Patent Publication No. 56-146,796 discloses a protective layer formed from a hydrophobic polymeric compound emulsion on a thermosensitive colored image-forming layer.

45 Japanese Unexamined Patent Publication No. 58-199,189 discloses an intermediate layer formed from a water-soluble polymeric compound solution or a hydrophobic polymeric compound emulsion on a thermosensitive colored image-forming layer, and a surface layer formed from a solution of a hydrophobic polymer in a solvent on the intermediate layer.

Japanese Unexamined Patent Publication Nos. 62-164,579 and 2-23,3149 disclose a thermosensitive colored image-forming layer containing an additive consisting of an epoxy compound and/or an aziridine compound.

50 In the thermosensitive colored image-forming layer containing the phenolic antioxidant, the resultant colored images exhibit a longer persistency in the ambient atmosphere than that of a conventional colored image-forming layer free from the phenolic antioxidant, but the improvement in the storage stability of the resultant colored images is still not satisfactory. Also, the phenolic antioxidant does not effectively enhance the resistance of the colored images to the oily or fatty substances and plasticizers. The resistance of the colored images to oily or fatty substance or plasticizer is determined in such a manner that an oily or fatty substance, for example, a salad oil, or a plasticizer, is brought into contact with colored images, the colored images are left in contact with the oily or fatty substance or the plasticizer for a predetermined time, and then a retention of

the color density of the tested colored images is measured in comparison with an initial color density thereof.

When the protective layer or the intermediate and surface layers are formed on the thermosensitive colored image-forming layer, the resultant colored images exhibit an enhanced storage stability in the ambient atmosphere, to a certain extent, but the fading of the colored images cannot be avoided after a lapse of a long time. Also, although the resistance of the colored images to the oily or fatty substances, or to the plasticizer, immediately after the contact with the oily or fatty substance, or the plasticizer, is improved, the colored images gradually fade with a lapse of time and a penetration of the oily or fatty substance, or the plasticizer, into the colored image-forming layer, and finally disappear. Therefore, the provision of the protecting layer or the intermediate and surface layer cannot completely eliminate this undesirable color-fading of the images.

The addition of the epoxy compound and/or aziridine compound to the colored image-forming layer is unsatisfactory in that it takes a long time to satisfactorily stabilize the colored images formed on the colored image-forming layer by a heat-recording operation, and therefore, if an oily or fatty substance, for example, salad oil, is brought into contact with the colored image-forming layer immediately after the heat-recording operation, the resultant colored images are faded to a great extent.

Also, when the epoxy compound is used together with a conventional phenolic color-developing agent, the resultant thermosensitive colored image-forming layer exhibits a lowered whiteness, and sometimes, is color-developed at a relatively low temperature of 50°C to 60°C which is lower than the temperature at which a heat recording operation is carried out.

This phenomenon is referred to as a low temperature ground color-developing phenomenon hereafter.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a thermosensitive recording material allowing colored images having an excellent storage persistency over a long time and a superior resistance to oil or fat substance, plasticizer, heat, and moisture, to be formed thereon.

Another object of the present invention is to provide a thermosensitive recording material having a satisfactory whiteness, thermosensitivity, and inhibition of a low temperature ground color-developing phenomenon.

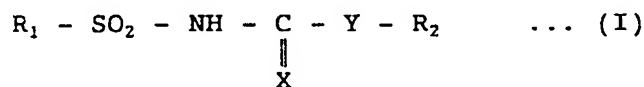
Still another object of the present invention is to provide a thermosensitive recording material useful for facsimile printers, word processor printers, video printers, CRT image-forming recording material, medical diagnosis, passenger's tickets, coupon tickets, and commuter's passes, which must have a high persistency in terms of the quality of the colored images recorded thereon, and for label sheets in a POS bar code price-indicating system, to be attached to an inside surface of a polyvinyl chloride film containing a plasticizing agent and wrapping fresh food or meat containing an oily or fatty substance, which label sheets are unavoidably brought into contact with the plasticizing agent and/or the oily or fatty substance.

The above-mentioned objects can be attained by the thermosensitive recording material of the present invention, which comprises

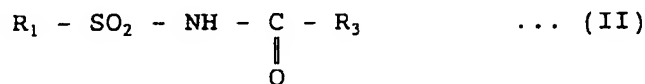
a sheet substrate, and

a thermosensitive colored image-forming layer formed on a surface of the sheet substrate and comprising a substantially colorless dye precursor, a color developing agent reactive with the dye precursor upon heating to thereby develop a color, and a binder,

the color developing agent comprising at least one aromatic sulfonyl (thio) amide compound selected from the group consisting of the compounds of the formulae (I) and (II):



and



in which formulae (I) and (II), X and Y, respectively and independently from each other, represent a member selected from the group consisting of oxygen and sulfur atoms; R₁ represents a member selected from the group

consisting of unsubstituted aromatic mono- and poly-cyclic groups, and substituted phenyl groups having at least one substituent selected from the group consisting of lower alkyl groups, aryl groups and halogen atoms; R_2 represents a member selected from the group consisting of substituted alkyl groups having at least one substituent selected from the group consisting of aralkyl and aryloxy groups, unsubstituted aromatic mono- and polycyclic groups, and substituted aromatic mono- and poly-cyclic groups having at least one substituent selected from the group consisting of alkyl, alkenyl, aryl, aralkyl, alkyloxy, aryloxy, aralkyloxy, alkylmercapto, arylmercapto, aralkylmercapto, alkyloxycarbonyl, aryloxycarbonyl and aralkyloxycarbonyl groups and halogen atoms; and R_3 represents a member selected from the group consisting of substituted phenyl groups having at least one substituent selected from the group consisting of lower alkyl groups, aryl groups and halogen atoms, unsubstituted aromatic mono- and poly-cyclic groups and aliphatic and cycloaliphatic hydrocarbon groups having 1 to 20 carbon atoms.

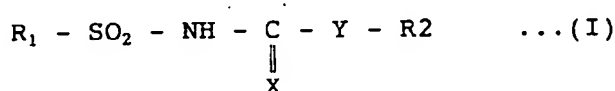
In an embodiment of the thermosensitive recording material of the present invention, the thermosensitive colored image-forming layer further contains a colored image-stabilizing agent comprising at least one member selected from the group consisting of aromatic compounds having at least one epoxy group and organic compounds, namely, aromatic, aliphatic and cycloaliphatic compounds, having at least one aziridinyl group.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

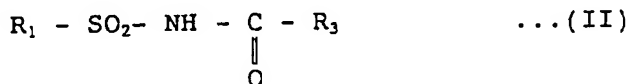
The thermosensitive recording material of the present invention comprises a sheet substrate and a thermosensitive colored image-forming layer formed on a surface of the sheet substrate.

The thermosensitive colored image-forming layer comprises a substantially colorless dye precursor, a color-developing agent reactive with the dye precursor upon heating, to thereby develop a color, and a binder.

In the present invention, the color developing agent must comprise at least one aromatic sulfonyl(thio)amide compound selected from N-arylsulfonyl(thio)carbamic acid esters the formula (I):



and N-arylcarbonylarylsulfonamides and N-alkylcarbonylarylsulfonamides of the formula (II):



In the formula (I), X and Y, respectively and independently from each other, represent a member selected from the group consisting of oxygen and sulfur atoms; R_1 represents a member selected from the group consisting of unsubstituted aromatic mono- and poly-cyclic groups, and substituted phenyl groups having at least one substituent selected from the group consisting of lower alkyl groups, aryl groups and halogen atoms; and R_2 represents a member selected from the group consisting of substituted alkyl groups having at least one substituent selected from the group consisting of aralkyl and aryloxy groups, unsubstituted aromatic mono- and polycyclic groups, and substituted aromatic mono- and polycyclic groups having at least one substituent selected from the group consisting of alkyl, alkenyl, aryl, aralkyl, alkyloxy, aryloxy, aralkyloxy, alkylmercapto, arylmercapto, aralkylmercapto, alkyloxycarbonyl, aryloxycarbonyl and aralkyloxycarbonyl groups and halogen atoms.

In the formula (II), R_1 is as defined above, and R_3 represents a member selected from the group consisting of substituted phenyl groups having at least one substituent selected from the group consisting of lower alkyl groups, aryl groups and halogen atoms, unsubstituted aromatic mono- and poly-cyclic groups and aliphatic and cycloaliphatic hydrocarbon groups having 1 to 20 carbon atoms. The aliphatic and cycloaliphatic hydrocarbon groups may be saturated or unsaturated. The cycloaliphatic hydrocarbon groups have 3 to 20 carbon atoms.

Although the aromatic sulfonyl(thio)amide compounds of the formulae (I) and (II) do not have an acid group, for example, a phenolic hydroxyl group or carboxyl group, nevertheless those aromatic sulfonyl(thio)amide compounds serve as a color-developing agent for the electron-donative dye-precursor in the thermosensitive colored image-forming layer.

Namely, even through the aromatic sulfonyl(thio)amide compounds of the formulae (I) and (II) are free from the above-mentioned phenolic hydroxyl group and carboxyl group, those compounds exhibit a strong color-

developing activity. The reason for the strong color-developing activity of the aromatic compounds of the formulae (I) and (II) is not completely clear, but it is assumed that, in the aromatic sulfon(thio)amide compounds of the formula (I) and (II), the thio(amide) group, $-NH(C=X)-$, is activated by a sulfonyl group, $-SO_2-$, adjacent thereto, to thus exhibit an color-developing property similar to that of the phenolic hydroxyl and carboxyl groups.

5 The N-arylsulfonyl(thio) carbamic acid esters of the formula (I) are preferably selected from:

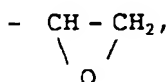
phenyl N-(p-toluenesulfonyl) carbamate (m.p.: 106°C)
 2,3,4-trimethylphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 144°C),
 benzyl N-(p-toluenesulfonyl) carbamate (m.p.: 98°C),
 2-phenoxyethyl N-(p-toluenesulfonyl) carbamate (m.p.: 120°C),
 10 p-cumylphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 120°C),
 o-biphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 136°C),
 1-naphthyl N-(p-toluenesulfonyl) carbamate (m.p.: 148°C),
 1-(4-methoxynaphthyl) N-(p-toluenesulfonyl) carbamate,
 p-benzyloxycarbonylphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 112 to 130°C),
 15 p-methoxycarbonylphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 176°C),
 p-n-butoxycarbonylphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 113°C),
 p-benzyloxyphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 122°C),
 m-benzyloxyphenyl N-(p-toluenesulfonyl) carbamate,
 p-methoxyphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 95°C),
 20 m-methoxyphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 96°C),
 p-ethoxyphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 88°C),
 p-n-butoxyphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 114°C),
 p-chlorophenyl N-(benzenesulfonyl) carbamate,
 2-methoxy-4-allylphenyl N-(p-toluenesulfonyl) carbamate (m.p.: 123°C),
 25 p-methylmercaptophenyl N-(p-toluenesulfonyl) carbamate (m.p.: 95°C),
 3-methyl-4-methylmercaptophenyl N-(p-toluenesulfonyl) carbamate (m.p.: 105°C),
 p-biphenyl N-(o-toluenesulfonyl) carbamate,
 p-benzylmercaptophenyl N-(p-toluenesulfonyl) carbamate,
 p-benzyl N-(1-naphthalenesulfonyl) carbamate,
 30 p-tolyl N-(p-toluenesulfonyl) thiocarbamate (m.p.: 95°C),
 p-methylbenzyl N-(p-toluenesulfonyl) dithiocarbamate,
 1-naphthyl N-(p-toluenesulfonyl) carbamate, and
 p-phenoxyphenyl N-(p-toluenesulfonyl) carbamate.

35 The N-arylcarbonylarylsulfonamides and N-alkylcarbonylarylsulfonamides of the formula (II) are preferably selected from:

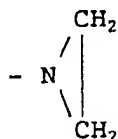
N-benzoylbenzenesulfonamide (m.p.: 147°C),
 N-(o-toluoyl) benzenesulfonamide (m.p.: 91°C),
 N-(m-toluoyl) benzenesulfonamide (m.p.: 116°C),
 N-(p-toluoyl) benzenesulfonamide (m.p.: 135°C),
 40 N-(1-naphthoyl) benzenesulfonamide (m.p.: 174°C),
 N-(2-naphthoyl) benzenesulfonamide (m.p.: 151°C),
 N-benzoyl-o-toluenesulfonamide (m.p.: 126°C),
 N-(o-toluoyl)-o-toluenesulfonamide (m.p.: 136°C),
 N-(m-toluoyl)-o-toluenesulfonamide (m.p.: 118°C),
 45 N-(p-toluoyl)-o-toluenesulfonamide (m.p.: 141°C),
 N-benzoyl-p-toluenesulfonamide (m.p.: 137°C),
 N-(o-toluoyl)-p-toluenesulfonamide (m.p.: 112°C),
 N-(m-toluoyl)-p-toluenesulfonamide (m.p.: 132°C),
 N-(p-toluoyl)-p-toluenesulfonamide (m.p.: 138°C),
 50 N-(3,4-dimethylbenzoyl)-p-toluenesulfonamide (m.p.: 147°C),
 N-(p-chlorobenzoyl)-p-toluenesulfonamide (m.p.: 195°C),
 N-(o-chlorobenzoyl)-p-toluenesulfonamide (m.p.: 111°C),
 N-(2,5-dichlorobenzoyl)-p-toluenesulfonamide (m.p.: 198°C),
 N-(1-naphthoyl)-p-toluenesulfonamide (m.p.: 150°C),
 55 N-(2-naphthoyl)-p-toluenesulfonamide (m.p.: 167°C),
 N-(3,4-dimethylbenzoyl)-3,4-dimethylbenzenesulfonamide (m.p.: 119°C),
 N-(benzoyl)-mesitylenesulfonamide,
 N-benzoyl-p-chlorobenzenesulfonamide (m.p.: 184°C),

N-(o-chlorobenzoyl)-1-naphthalenesulfonamide (m.p.: 177°C),
 N-(o-toluoyl)-2-naphthalenesulfonamide (m.p.: 145°C),
 N-(m-toluoyl)-2-naphthalenesulfonamide (m.p.: 147°C),
 N-(p-toluoyl)-2-naphthalenesulfonamide (m.p.: 166°C),
 N-acetyl-benzenesulfonamide (m.p.: 127°C),
 N-cyclohexanecarbonyl-p-toluenesulfonamide,
 N-lauoyl-p-toluenesulfonamide (m.p.: 83°C),
 N-myristoyl-p-toluenesulfonamide (m.p.: 90°C),
 N-palmitoyl-p-toluenesulfonamide (m.p.: 102°C),
 N-stealoyl-p-toluenesulfonamide (m.p.: 99°C),
 N-oleoyl-p-toluenesulfonamide, and
 N-acetylmesitylenesulfonamide (m.p.: 166°C).

In an embodiment of the thermosensitive recording material of the present invention, the thermosensitive colored image-forming layer contains a colored image-stabilizing agent comprising at least one member selected from aromatic compounds having at least one epoxy group of the formula:



as disclosed in Japanese Unexamined Patent Publication Nos. 62-164,579, and 2-220,885 and organic compounds having at least one aziridinyl group of the formula:



The aromatic compounds having at least one epoxy group and usable for the present invention are preferably selected from the group consisting of 4,4'-bis(2'',3''-epoxypropyloxy)diphenylsulfone, 2,2-bis[4'-(2'',3''-epoxypropyloxy)phenyl]propane, 1,4-bis(2'',3''-epoxypropyloxy)benzene, 4-(2''-methyl-2'',3''-epoxypropyloxy)-4'-benzyloxy-diphenylsulfone, 4-(2''-3''-epoxypropyloxy)-4'-(p-methylbenzyloxy)-diphenylsulfone, epoxidized o-novolac cresol resins, 4,4'-bis(2'',3''-epoxypropyloxy)diphenylmethane, 4,4'-bis(2'',3''-epoxypropylamino)diphenylmethane, bis(2'',3''-epoxypropyl)-4,4'-methylene dibenzoate, 4,4'-bis(2'',3''-epoxypropyloxy) biphenyl, 4,4'-bis(2'',3''-epoxypropyloxy)-3,3',5,5'-tetramethylbiphenyl, 2,6-bis(2',3'-epoxypropyloxy) naphthalene, and bis(2,3-epoxypropyl)terephthalate.

The organic compounds having at least one aziridinyl group are preferably selected from the group consisting of 2,4-bis(1-aziridinylcarbonylamino)toluene, bis[4-(1-aziridinylcarbonylamino)phenyl]methane, bis[3-chloro-4-(1-aziridinylcarbonylamino)phenyl]methane, 2,2-bis[4-(1-aziridinylcarbonyloxy)phenyl]propane, 1,4-bis(1-aziridinylcarbonyl)benzene.

The dye precursor usable for the present invention comprises at least one member selected from conventional triphenylmethane, fluoran and diphenylmethane leuco dyes, for example, 3-(4-diethylamino-2-ethoxyphenyl)-3-(1-ethyl-2-methylindole-3-yl)-4-azaphthalide, crystal violet lactone, 3-(N-ethyl-N-isopentylamino)-6-methyl-7-anilino-fluoran, 3-diethylamino-6-methyl-7-anilino-fluoran, 3-diethylamino-6-methyl-7-(2',4'-dimethyl-anilino) fluoran, 3-(N-ethyl-N-p-toluidino)-6-methyl-7-anilino-fluoran, 3-pyrrolidino-6-methyl-7-anilino-fluoran, 3-dibutylamino-6-methyl-7-anilino-fluoran, 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilino-fluoran, 3-diethylamino-7-(o-chloroanilino) fluoran, 3-dibutylamino-7-(o-chloroanilino) fluoran, 3-diethylamino-7-(m-trifluoromethyl-anilino) fluoran, 3-diethylamino-6-methyl-7-chloro-fluoran, 3-diethylamino-6-methyl-fluoran, 3-cyclohexylamino-6-chloro-fluoran and 3-(N-ethyl-N-hexylamino)-6-methyl-7-(p-chloroanilino) fluoran.

The color-developing agent usable for the present invention optionally comprises, in addition to the aromatic sulfon(thio)amide compound, at least one conventional acid compound selected from phenolic compounds and organic acid compounds, for example, 2,2-bis(4-hydroxyphenyl) propane(bisphenol A), 1,1-bis(4-hydroxyphenyl)-1-phenyl-ethane, 1,4-bis[1-methyl-1-(4'-hydroxy-phenyl)ethyl] benzene, 1,3-bis[1-methyl-1-(4'-hydroxyphenyl)ethyl] benzene, dihydroxydiphenylether (JP-A-1-180,382), benzyl p-hydroxybenzoate (JP-A-52-140,483), bis-phenol S, 4-hydroxy-4'-iso propyloxydiphenyl-sulfone(JP-A-60-13,852), 1,1-di(4-hydroxy-

phenyl) cyclohexane, 1,7-di(4-hydroxy-phenylthio)-3,5-dioxaheptane(JP-A-59-52,694), 3,3'-diallyl-4,4'-dihydroxydiphenyl-sulfone(JP-A-60-208,286).

Preferably, in the color-developing agent, the aromatic sulfonyl(thio)amide compound is present in an amount of 50% to 100% based on the total weight of the color-developing agent.

5 The thermosensitive colored image-forming layer of the present invention optionally further comprises a heat-fusible organic substance, usually referred to as a sensitizing agent. This sensitizing agent comprises at least one organic compound having a melting point of from 50°C to 160°C, for example, phenyl 1-hydroxy-2-naphthoate (JP-A-57-191,089), p-benzyl-biphenyl (JP-A-60-82,382), benzyl-naphthylether (JP-A-58-87,094), dibenzyl terephthalate (JP-A-58-98,285), benzyl p-benzoyloxybenzoate (JP-A-57-201,691), diphenyl carbonate, 10 ditolyl carbonate (JP-A-58-136,489), m-terphenyl (JP-A-57-89,994), 1,2-bis(m-tolyloxy) ethane (JP-A-60-56,588), 1,5-bis (p-methoxyphenoxy)-3-oxapentane (JP-A-62-181,183), oxalic acid diesters (JP-A-64-1,583) and 1,4-bis(p-tolyloxy) benzene (JP-A-2-153,783).

The thermosensitive colored image-forming layer of the present invention optionally further comprises at least one member selected from hindered phenolic compounds and ultraviolet ray-absorbers, as disclosed, for 15 example, in JP-A-57-151,394, JP-A-58-160,191, JP-A-58-69,096, JP-A-59-2,884, JP-A-59-95,190, JP-A-60-22,288, JP-A-60-255,485, JP-A-61-44,686, JP-A-62-169,683, JP-A-63-17,081, and JP-A-1-249,385.

The phenolic compounds and ultraviolet ray-absorbers are preferably selected from 1,1,3-tris(3'-cycloxy-4'-hydroxyphenyl)butane; 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 4,4'-thio-bis(3-methyl-6-tert-butylphenol), 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 2,2'-dihydroxy-4,4'-dime- 20 thoxybenzophenone, p-octylphenyl salicylate, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, ethyl 2-cyano-3,3'-diphenyl acrylate, and tetra(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxate.

As stated above, in the thermosensitive recording material of the present invention, the thermosensitive colored image-forming layer comprises a dye precursor, a color-developing agent comprising at least one aromatic sulfonyl(thio)amide compound the formulae (I) and/or (II), a binder, and optionally, a colored image- 25 stabilizing agent comprising at least one member selected from the epoxy group-having aromatic compounds and the aziridinyl group-having organic compounds.

The thermosensitive colored image-forming layer of the present invention optionally further contains an additive comprising at least one member selected from, for example, conventional color-developing phenolic and organic acid compounds, sensitizing agents, antioxidants, ultraviolet ray-absorbers, waxes, and organic 30 and inorganic pigments.

In the thermosensitive colored image-forming layer of the present invention, preferably, the dye precursor is present in an amount of 5 to 40% by weight, the color-developing aromatic sulfonyl(thio)amide compound is present in an amount of 10 to 50% by weight, and the binder is present in an amount of 5 to 20% by weight. The above-mentioned amounts are based on the total dry weight of the thermo sensitive colored image-forming 35 layer. If the amount of the color-forming aromatic sulfonyl(thio)amide compound is less than 10% by weight, the resultant colored image-forming layer sometimes exhibits an unsatisfactory color-developing effect. Also, an amount of the color-developing aromatic sulfonyl(thio)amide compound exceeding 50% by weight is not effective for further increasing the color-developing power of the resultant color image-forming layer.

Preferably, the colored image-stabilizing agent comprising the epoxy group-having aromatic compound and/or the aziridinyl group-having organic compound, is present in an amount of 1 to 30% by weight in the ther- 40 mosensitive colored image-forming layer.

The presence of the colored image-stabilizing agent in an amount of less than 1% does not impart a satisfactorily high persistency to the resultant colored images, and an amount of the colored image-stabilizing agent of more than 30% by weight does not effectively further enhance the storage durability of the resultant colored 45 images.

The antioxidant or ultraviolet ray absorber is optionally preferably contained in an amount of 1 to 10% by weight in the thermosensitive colored image-forming layer. An amount of the antioxidant or ultraviolet ray absorber of less than 1% by weight does not satisfactorily and effectively prevent a fading or discoloring of the colored 50 images. Further, an amount of more than 30% by weight of the antioxidant or ultraviolet ray absorber causes a reduction of the whiteness of the resultant colored image-forming layer, and sometimes hinders the ease of travel of the resultant recording material in a printer.

The conventional color-developing phenolic or organic acid compound is optionally preferably contained in an amount of 5 to 40% in the colored image-forming layer.

The sensitizing agent is optionally preferably contained in an amount of 10 to 40% by weight, and the wax and organic or inorganic pigment are optionally contained in amounts of 5 to 20% by weight and 10 to 50% by 55 weight, respectively.

The wax usable for the present invention preferably comprises at least one member selected from, for example, paraffin waxes, carnauba wax, microcrystalline waxes, polyethylene waxes, amide type waxes, bis-

mide type waxes, higher fatty acid amide waxes, for example, stearic acid amide, ethylene-bis-stearoamide wax, higher fatty acid esters and metal salts, for example, zinc stearate, aluminum stearate calcium stearate and zinc oleate.

The inorganic and organic pigments usable for the present invention are preferably selected from inorganic fine particles of, for example, calcium carbonate, silica, zinc oxide, titanium dioxide, aluminum hydroxide, zinc hydroxide, barium sulfate, clay, anhydrous clay, talc, and surface-treated calcium carbonate and silica and organic fine particles of, for example, urea-formaldehyde resins, styrene-methacrylate copolymer resins and polystyrene resins.

The binder preferably comprises at least one member selected from water-soluble polymeric materials, for example, various types of polyvinyl alcohol resins which have a different molecular weight from each other, starch and starch derivatives, cellulose derivatives, for example, methoxy cellulose, carboxymethyl cellulose, methyl cellulose and ethyl cellulose, sodium polyacrylate, polyvinyl pyrrolidone, acrylic acid amide-acrylic acid ester copolymers, acrylic acid amide-acrylic acid ester-methacrylic acid terpolymers, alkali salts of styrene-maleic anhydride copolymers, polyacrylic acid amide, sodium alginate, gelatine and casein, and water-insoluble polymeric materials, for example, polyvinyl acetate resins, polyurethane resins, styrene-butadiene copolymer resins, polyacrylic acid resins, polyacrylic acid ester resins, vinyl chloride-vinyl acetate copolymer resins, polybutyl acrylate, ethylene-vinyl acetate copolymer resins and styrene-butadiene-acrylic compound-terpolymer resins, which are used in the form of latexes.

The sheet substrate usable for the present invention is not limited to a specific group of materials, and usually the sheet substrate comprises a member selected from fine paper sheets, coated paper sheet having a clay or plastic coating layer, cast-coated paper sheets, paper boards, plastic resin films, synthetic paper sheets comprising a plastic resin, and laminated paper sheets. Preferably, the sheet substrate has a basis weight of 40 to 170 g/m².

The colored image-forming layer can be formed on a surface of a sheet substrate, by applying a coating liquid containing the above-mentioned components, and by drying and solidifying the coating liquid layer on the sheet substrate.

The colored image-forming layer is preferably present in a dry weight of from 1 to 15 g/m², more preferably 2 to 10 g/m².

In the present thermosensitive recording material, a protective layer and/or a printed layer may be formed on the colored image-forming layer.

EXAMPLES

The present invention will be further explained by the following specific examples, which are merely representative and do not in any way restrict the scope of the present invention.

Synthesis Example 1 Preparation of N-(o-toluoyle)-p-toluenesulfonamide

A three necked flask equipped with a dropping funnel, a thermometer, and a reflux condenser was charged with 10 g of p-toluenesulfonamide. The p-toluene-sulfonamide was dissolved in 20 ml of pyridine, and to the resultant reaction solution were dropwise added 9.5 g of o-toluoyle chloride, while the flask was cooled in an ice bath, and the reaction mixture was stirred by using a magnetic stirrer. This dropwise addition was carried out at a temperature of 20°C or less, and after the dropwise addition was completed, the temperature of the reaction mixture was gradually restored to room temperature. The ice bath was then replaced by a heating oil bath, and the flask placed in the heating oil bath to heat the reaction mixture at a temperature of 140°C for 3 hours. After the reaction was completed, the resultant reaction product was washed with 1N hydrochloric acid solution and extracted with ethyl ether. The extracted ethyl ether solution was washed with water, dried over magnesium sulfate, and filtered, and the resultant filtered solution was solidified by evaporating away ethyl ether, to obtain 13 g of light yellow crystals as the product.

The crystals were recrystallized by using toluene, and a white crystalline substance was obtained in an amount of 12 g, and exhibited a melting point of 118°C.

It was confirmed by NMR measurement and mass spectrometry (chemical ionization method) that the resultant product was the intended N-(o-toluoyle)-p-toluenesulfonamide.

Synthesis Example 2 Preparation of N-benzoyl-o-toluenesulfonamide

The same synthesis procedures as in Synthesis Example 1 were carried out except that the p-toluenesulfonamide was replaced by o-toluenesulfonamide and 9.5 g of the o-toluoyle chloride was replaced by 8.5 g of

benzoyl chloride, whereby a white crystalline substance having a melting point of 126°C was obtained, which was subjected to NMR measurement and a mass spectrometry (chemical ionization method), whereby the resultant product was identified as the intended N-(o-toluoyl)benzenesulfonamide.

5 Synthesis Example 3 Preparation of N-(o-toluoyl) benzenesulfonamide

The same synthesis procedures as in Synthesis Example 1 were carried out except that p-toluenesulfonamide was replaced by o-toluenesulfonamide and the o-toluoyl chloride was employed in an amount of 10 g in place of 9.5 g, whereby 10 g of white crystals having a melting point of 91°C was obtained.

10 Thereafter, when subjected to NMR measurement and a mass spectrometry (chemical ionization method), it was confirmed that the resultant crystals were the intended N-(o-toluoyl)benzenesulfonamide.

Synthesis Example 4 Preparation of N-palmitoyl-p-toluenesulfonamide

15 The same synthesis procedures as in Synthesis Example 1 were carried out except that 9.5 g of o-toluoyl chloride were replaced by 18.5 g of palmitoyl chloride, whereby 16 g of white crystals having a melting point of 102°C was obtained.

Thereafter, when subjected to NMR measurement and a mass spectrometry (chemical ionization method), it was confirmed that the obtained crystals were the intended N-palmitoyl-p-toluenesulfonamide.

20

Synthesis Example 5 Preparation of phenyl N-(p-toluenesulfonyl)-carbamate

A three necked flask equipped with a dropping funnel, a thermometer and a reflux condenser was charged with 10 g of p-toluenesulfonamide. The p-toluenesulfonamide was dissolved in 20 ml of pyridine, and to the resultant reaction solution was dropwise added a solution of 8.7 g of phenyl chlorocarbonate in 10 ml of toluene, while the flask was cooled in an ice bath and the reaction mixture was stirred by using a magnetic stirrer. This dropwise addition was carried out at a temperature of 20°C or less. After the dropwise addition was completed, the temperature of the reaction mixture was gradually restored to room temperature, and then the ice bath was replaced by a heating oil bath, and the flask was placed in the heating oil bath to heat the reaction mixture at a temperature of 100°C for 3 hours. After the reaction was completed, the resultant reaction product was washed with 1N hydrochloric acid solution and extracted with ethyl ether. The extracted ethyl ether solution was washed with water, dried over magnesium sulfate, and filtered, and the ethyl ether in the resultant filtered solution was evaporated to obtain a toluene solution of the reaction product. A small amount of fresh toluene was added to the toluene solution, and the solution was subjected to a recrystallization process. The product was 11.5 g of white crystals having a melting point of 106°C.

35 Thereafter, it was confirmed by NMR measurement and a mass spectrometry (chemical ionization method) that the resultant product was the intended phenyl N-(p-toluenesulfonyl)-carbamate.

Synthesis Example 6 Preparation of benzyl N-(p-toluenesulfonyl)-carbamate

40

The same synthesis procedures as in Synthesis Example 5 were carried out except that 8.7 g of phenyl chlorocarbonate were replaced by 9.6 g of benzyl chlorocarbonate, whereby 14.1 g of white crystals having a melting point of 98°C was obtained.

45 Thereafter, it was confirmed by NMR measurement and an IR measurement that the obtained crystals were the intended benzyl N-(p-toluenesulfonyl)-carbamate.

Synthesis Example 7 Preparation of p-benzyloxy-phenyl N-(p-toluenesulfonyl)carbamate

50 A three necked flask equipped with a dropping funnel, a thermometer and a reflux condenser was charged with 5.0 g of hydroquinone-monobenzylether. The hydroquinone monobenzyl ether was dissolved in 20 ml of toluene at a temperature of 80°C, and to the resultant reaction solution was dropwise added 5.2 g of p-toluenesulfonyl isocyanate. After the dropwise addition was completed, several drops of pyridine were added to the reaction mixture, and the resultant reaction mixture was maintained at a temperature of 80°C for 2 hours. After the reaction was completed, the resultant reaction product was cooled, to cause the reaction product to crystallize and precipitate, and the precipitated white crystals were filtered and dried, whereby 9.4 g of white crystals having a melting point of 122°C was obtained.

55 Thereafter, it was confirmed by NMR measurement and IR measurement that the resultant product was the intended p-benzyloxyphenyl N-(p-toluenesulfonyl)carbamate.

Example 1

A thermosensitive recording paper sheet was prepared by the following procedures.

5 (1) Preparation of an aqueous dye precursor dispersion A in the following composition

	<u>Component</u>	<u>Part by weight</u>
10	3-(N-isopentyl-N-ethylamino)- 6-methyl-7-anilinofluoran	20
	10% aqueous solution of polyvinyl alcohol	10
15	Water	70

The composition was dispersed in a sand grinder to an extent such that the resultant dispersed solid particles had an average size of 1 μ m or less.

20 (2) Preparation of an aqueous color-developing agent dispersion B in the following composition

	<u>Component</u>	<u>Part by weight</u>
25	N-(o-toluoyl)-p-toluenesulfonamide	20
	10% aqueous solution of polyvinyl alcohol	10
30	Water	70

35 The composition was dispersed in a sand grinder to an extent such that the resultant dispersed solid particles had an average size of 1 μ m or less.

(3) Preparation of a pigment coated paper sheet

40 A coating liquid was prepared by mixing an aqueous dispersion, prepared by dispersing 85 parts by weight of anhydrous clay available under the trademark of Ansilex, from Engelhard Corporation, in 320 parts by weight of water, with 40 parts by weight of an aqueous emulsion of a styrene - butadiene copolymer in a solid concentration of 50% by weight and 50 parts by weight of a 10% aqueous oxidized starch solution.

The coating liquid was coated on a surface of a fine paper sheet having a basis weight of 48 g/m², to form a coating layer having a dry weight of 7.0 g/m², whereby coated paper sheet was obtained.

45 (4) Formation of thermosensitive colored image - forming layer

50 A coating liquid was prepared by evenly mixing 80 parts by weight of the aqueous dye precursor dispersion A and 160 parts by weight of the aqueous color-developing agent dispersion B with 30 parts by weight of a calcium carbonate pigment, 20 parts by weight of a 25% aqueous zinc stearate dispersion, 15 parts by weight of a 30% aqueous paraffin dispersion, and 120 parts by weight of a 10% aqueous polyvinyl alcohol solution, by agitating the mixture.

55 A surface of the pigment coated paper sheet was coated with the resultant coating liquid and dried. A thermosensitive colored image-forming layer was formed in a weight of 5.0 g/m², to provide a thermosensitive recording paper sheet.

The recording sheet was treated by a super calender, and the calendered surface of the recording sheet had a Bekk smoothness of 600 to 1000 seconds.

A specimen of the resultant thermosensitive recording sheet was tested by a thermal inclination tester made

by Toyoseiki Co., at a temperature of 120°C under a pressure of 2.5 kg/cm² for one second, to color develop the thermosensitive colored image-forming layer thereof, and as a result, a clear black colored image was found to have a high color density of more than 1.2 as determined by Macbeth Reflection Color Density Tester - 914 (trademark), as shown in Table 1. The non-color developed portions of the tested colored image-forming layer were subjected to a whiteness test by using a Hunter Whiteness Tester (trademark) with a blue filter.

The test results are shown in Table 1.

Example 2

The same procedures as in Example 1 were carried out except that, in the preparation of the aqueous color developing agent dispersion B, N-(o-toluoyl)-p-toluenesulfonamide was replaced by N-benzoyl-o-toluenesulfonamide.

The test results are shown in Table 2.

Example 3

The same procedures as in Example 1 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B, N-(o-toluoyl)-p-toluenesulfonamide was replaced by N-benzoyl-o-toluenesulfonamide.

The test results are shown in Table 1.

Comparative Example 1

The same procedures as in Example 1 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B, N-(o-toluoyl)-p-toluenesulfonamide was replaced by a conventional color-developing agent consisting of 2,2-bis(4-hydroxyphenyl)propane, namely bisphenol A.

The test results are shown in Table 1.

Table 1

Item Example No.	Color density(D) of color-developed portion		Whiteness(%) of non-color developed portion	
Example	1	1.22	85.4	
	2	1.20	85.6	
Comparative Example 1	1.20		70.0	

Example 3

The same procedures as in Example 1 were carried out, with the following exception.

(1) An aqueous dispersion C of a colored image-stabilizing agent was prepared in the following composition.

Component	Part by weight
Bis[4-(1-azinidinylcarbonylamino) phenyl] methane	20
10% aqueous solution of polyvinyl alcohol	10
Water	70

The mixture was ground in a sand grinder to an extent such that the resultant solid particle had an average size of 1 μm or less.

(2) A coating liquid was prepared by mixing 50 parts by weight of the aqueous dye precursor dispersion A, 100 parts by weight of the aqueous color-developing agent dispersion B and 100 parts by weight of the aqueous colored image-stabilizing agent dispersion C with 30 parts by weight of a calcium carbonate pigment, 20 parts by weight of a 25% zinc stearate dispersion, 15 parts by weight of a 30% paraffin dispersion and 120 parts by weight of a 10% polyvinyl alcohol solution, while stirring.

(3) As a result of the same color-developing test as in Example 1, clear black colored images having a color density of 1.0 or more, as shown in Table 2, were obtained.

(4) The color-developed specimen was immersed in a salad oil within 30 minutes from the completion of the color-developing operation or 5 hours after the completion of the color-developing operation, and left to stand at room temperature for 24 hours. Thereafter, the color density of the colored images retained in the thermosensitive colored-image-forming layer was measured by Macbeth Reflection Color Density Tester.

The test results are shown in Table 2.

Example 4

The same procedures as in Example 3 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B, N-(0-toluoyl)-p-toluenesulfonamide was replaced by N-benzoyl-o-toluenesulfonamide.

The test results are shown in Table 2.

Example 5

The same procedures as in Example 3 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B, N-(o-toluoyl)-p-toluenesulfonamide was replaced by N-palmitoyl-p-toluenesulfonamide.

The test results are shown in Table 2.

Example 6

The same procedures as in Example 3 were carried out except that, in the preparation of the aqueous colored image-stabilizing agent dispersion C, bis[4-(1-aziridinylcarbonylamino)phenyl]methane was replaced by 2,4-bis(1-aziridinylcarbonylamino)toluene.

The test results are shown in Table 2.

Example 7

The same procedures as in Example 3 were carried out, with the following exceptions.

(1) The coating liquid for the colored image-forming layer was prepared by mixing 40 parts by weight of the aqueous dye precursor dispersion A, 80 parts by weight of the aqueous color-developing agent dispersion B and 70 parts by weight of the aqueous colored image-stabilizing agent dispersion C with 40 parts by weight of a calcium carbonate pigment, 20 parts by weight of a 25% zinc stearate dispersion, 15 parts by weight of a 30% paraffin dispersion and 120 parts by weight of a 10% polyvinyl alcohol solution, while stirring.

The coating liquid was applied to a surface of a fine paper sheet having a basis weight of 48 g/m², to form a thermosensitive colored image-forming layer having a dry weight of 7.0 g/m².

The test results of the resultant thermosensitive recording sheet are shown in Table 2.

Example 8

The same procedures as in Example 3 were carried out except that, in the preparation of the aqueous dye precursor dispersion A, 3-(N-isopentyl-N-ethylamino)-6-methyl-7-anilino-fluoran was replaced by 3-dibutylamino-6-methyl-7-anilino-fluoran.

The test results of the resultant thermosensitive recording sheet are shown in Table 2.

Comparative Example 2

The same procedures as in Example 3 were carried out except that, in the preparation of the aqueous color-developing agent dispersion, N-(o-toluoyl)-p-toluenesulfonamide was replaced by 2,2-bis(4-hydroxyphenyl)propane, namely bisphenol A.

The test results of the resultant thermosensitive recording sheet are shown in Table 2.

Comparative Example 3

The same procedures as in Comparative Example 1 were carried out except that the resultant thermosensitive recording sheet was subjected to the same salad oil resistance tests as in Example 3.

The test results are shown in Table 2.

Table 2

Example No.	Item	Color density (D) of colored image	Color density (D') of remaining colored image after immersion test in salad oil	
			Immersed within 30 minutes from color-development	Immersed 5 hours after color-development
Example	3	1.20	1.00	1.12
	4	1.16	0.96	1.06
	5	1.10	0.90	1.02
	6	1.22	1.01	1.12
	7	1.12	0.98	1.03
	8	1.10	0.95	1.00
Comparative Example	2	1.15	0.26	0.97
	3	1.22	0.13	0.13

Example 9

The same procedures as in Example 1 were carried out, with the following exceptions.

(1) The aqueous color-developing agent dispersion B was replaced by an aqueous color-developing agent dispersion B-a having the following composition.

Composition of dispersion B-a

<u>Component</u>	<u>Part by weight</u>
p-cumylpheny N-(p-toluenesulfonyl) carbamate (m.p.=120°C)	20
10% aqueous polyvinyl alcohol solution	10
Water	70

(2) A coating liquid was prepared by mixing 75 parts by weight of the aqueous dye precursor dispersion A and 150 parts by weight of the aqueous color-developing agent dispersion B-a with 33 parts by weight of a calcium carbonate pigment, 20 parts by weight of a 25% zinc stearate dispersion, 15 parts by weight of

a 30% paraffin dispersion, and 120 parts by weight a 10% polyvinyl alcohol solution, while stirring.

(3) The coating liquid was applied to a surface of the pigment-coated paper sheet mentioned in Example 1, to form a thermosensitive colored image-forming layer having a dry weight of 5.0 g/m².

(4) After calendering in the same manner as in Example 1, the resultant thermosensitive recording sheet was subjected to a colored image-forming test by using a dynamic color-forming tester prepared by modifying a thermosensitive facsimile printing machine made by Hitachi Seisakusho, at an applied energy of 0.46 mj/dot.

The color density (D) of the resultant colored image was measured by using a Macbeth Reflection Color Density Tester RD - 914 (Trademark).

The whiteness of the non-colored portion of the tested recording sheet was measured by using a Hunter Whiteness Tester with a blue filter.

The test results are shown in Table 3.

Example 10

The same procedures as in Example 9 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl)carbamate having a melting point of 120°C was replaced by p-benzyloxyphenyl N-(p-toluenesulfonyl)carbamate having a melting point of 126°C.

The test results are shown in Table 3.

Comparative Example 4

The same procedures as in Example 9 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl)carbamate was replaced by 2,2-bis(4-hydroxyphenyl)propane, namely bisphenol A, having a melting point of 156°C.

The test results are shown in Table 3.

Comparative Example 5

The same procedures as in Example 9 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl)carbamate (m.p.=120°C) was replaced by the 4-tert-butylphenyl N-phenyl-carbomate disclosed in JP-A-60-184, 879.

The test results are shown in Table 3.

Table 3

Example No.	Item	Color density (D) of colored image	Whiteness of non-colored portion (%)
Example	9	1.40	84.5
	10	1.41	85.6
Comparative Example	4	1.35	71.2
	5	0.55	85.0

Example 11

The same procedures as in Example 9 were carried out, with the following exceptions.

(1) A coating liquid was prepared by mixing 50 parts by weight of the aqueous dye precursor dispersion A, 150 parts by weight of the aqueous color-developing agent dispersion B-a and 50 parts by weight of the aqueous colored image-stabilizing agent dispersion C as mentioned in Example 3, with 30 parts by weight of a calcium carbonate pigment, 20 parts by weight of a 25% zinc stearate dispersion, 15 parts by weight of a 30% paraffin dispersion, and 120 parts by weight of a 10% polyvinyl alcohol solution.

(2) The color-developed specimens of the resultant thermosensitive recording sheet were subjected to the

same salad oil resistance test as mentioned in Example 3.
The test results are shown in Table 4.

Example 12

The same procedures as in Example 11 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl) carbamate having a melting point of 120°C was replaced by p-benzyloxyphenyl N-(p-toluenesulfonyl) carbamate having a melting point of 126°C.
The test results are shown in Table 4.

Example 13

The same procedures as in Example 11 were carried out except that, in the preparation of the aqueous colored image-stabilizing agent dispersion C, bis[4-(1-aziridinylcarbonylamino)phenyl]methane was replaced by 2,4-bis(1-aziridinyl-carbonylamino)toluene.
The test results are shown in Table 4.

Example 14

The same procedures as in Example 12 were carried out, with the following exceptions.

(1) The coating liquid for the thermosensitive colored image-forming layer was prepared by mixing 40 parts by weight of the aqueous dye precursor dispersion A, 120 parts by weight of the aqueous color-developing agent dispersion B-a and 40 parts by weight of the aqueous colored image-stabilizing agent dispersion with 40 parts by weight of a calcium carbonate pigment, 20 parts by weight of a 25% zinc stearate dispersion, 15 parts by weight of a 30% paraffin dispersion and 120 parts by weight of a 10% polyvinyl alcohol solution, while stirring.

(2) The coating liquid was applied to a surface of a fine paper sheet having a basis weight of 48 g/m², to form a thermosensitive colored image-forming layer having a dry weight of 7.0 g/m².

The test results are shown in Table 4.

Example 15

The same procedures as in Example 12 were carried out except that, in the preparation of the aqueous dye precursor dispersion A, 3-(N-isopentyl-N-ethylamino)-6-methyl-7-anilino-1-fluoro-2-naphthol was replaced by 3-dibutylamino-6-methyl-7-anilino-1-fluoro-2-naphthol.

The test results are shown in Table 4.

Comparative Example 6

The same procedures as in Example 11 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl)carbamate having a melting point of 120°C was replaced by 2,2-bis(4-hydroxyphenyl)propane, namely bisphenol A.

The test results are shown in Table 4.

Comparative Example 7

The same procedures as in Example 11 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl)carbamate having a melting point of 120°C was replaced by 4-tert-butylphenyl N-phenylcarbamate as disclosed in JP-A-60-184,874.

The test results are shown in Table 4.

Table 4

Example No.	Item	Color density (D) of colored image	Color density (D') of remaining color image after immersion test in salad oil	
			Immersed within 30 minutes after color-development	Immersed 5 hours after color-development
Example	11	1.32	1.21	1.28
	12	1.35	1.25	1.30
	13	1.30	1.15	1.25
	14	1.27	1.10	1.18
	15	1.28	1.16	1.22
Comparative Example	6	1.28	0.36	1.11
	7	0.47	0.13	0.35

Example 16

The same procedures as in Example 9 were carried out, with the following exceptions.

(1) An aqueous colored image-stabilizing agent dispersion C-a was prepared in the following composition and in the same manner as in Example 3.

Composition of dispersion C-a

<u>Component</u>	<u>Part by weight</u>
4,4'-bis(2",3"-epoxypropyloxy) diphenylsulfone	20
10% polyvinyl alcohol solution	10
Water	70

(2) A coating liquid was prepared by mixing 50 parts by weight of the aqueous dye precursor dispersion A, 150 parts by weight of the aqueous color-developing agent dispersion B-a and 50 parts by weight of the aqueous colored image-stabilizing agent dispersion C-a, with 30 parts by weight of a calcium carbonate pigment, 20 parts by weight of a 25% zinc stearate dispersion, 15 parts by weight of a 30% parafin dispersion and 120 parts by weight of a 10% polyvinyl alcohol solution, while stirring.

(3) The coating liquid was applied to a surface of the same pigment-coated paper sheet as in Example 1, to form a thermosensitive colored image-forming layer having a weight of 5.0 g/m², and the resultant thermosensitive recording sheet was calendared in the same manner as in Example 1.

(4) A specimen of the calendared thermosensitive recording sheet was subjected to a whiteness measurement by using a Hunter Whiteness Tester with a blue filter.

(5) Separately, a specimen of the calendared thermosensitive recording sheet was stored in a dryer controlled to a temperature of 60°C, for 24 hours, and then the whiteness of the resultant recording sheet was measured by using a Macbeth Reflection Color Density Tester RD-914 (trademark). The resultant measured color density is referred to as a low temperature ground color-formation value.

(6) Separately, a specimen of the recording sheet was subjected to the same colored image-forming test as in Example 11. The resultant measured color density value D is referred to as an initial color density value.

(7) The color image-formed recording sheet was subjected to the same salad oil-immersion test as in Example 3, except that the immersion of the colored image-formed recording sheet in the salad oil was

carried out immediately after the completion of the color development, at room temperature for 24 hours.

The color density of the remaining colored image was measured by a Macbeth Reflection Color Density Tester. The measured color density value is referred to as an after test color density value D' .

The retention R of the color density of the colored image is calculated in accordance with the following equation:

$$R(\%) = \frac{D'}{D} \times 100$$

The test results are shown in Table 5.

Example 17

The same procedures as in Example 16 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl)carbamate having a melting point of 120°C was replaced by p-benzyloxyphenyl N-(p-toluenesulfonyl)carbamate having a melting point of 126°C.

The test results are shown in Table 5.

Example 18

The same procedures as in Example 16 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl) carbamate having a melting point of 120°C was replaced by N-(o-toluoyl)-p-toluenesulfonamide having a melting point of 118°C.

The test results are shown in Table 5.

Example 19

The same procedures as in Example 17 were carried out except that, in the preparation of the aqueous colored image-stabilizing agent dispersion C-a, 4,4'-bis(2'',3''-epoxypropyloxy)diphenylsulfone was replaced by bis(2,3-epoxypropyl)terephthalate.

The test results are shown in Table 5.

Example 20

The same procedures as in Example 17 were carried out except that, in the preparation of the aqueous colored image-stabilizing agent dispersion C-a, 4,4'-bis(2'',3''-epoxypropyloxy)diphenylsulfone was replaced by 4-(2'-methyl-2',3'-epoxypropyloxy)-4'-benzyloxy-diphenylsulfone.

The test results are shown in Table 5.

Example 21

The same procedures as in Example 16 were carried out except that, in the preparation of the aqueous colored image-stabilizing agent dispersion C-a, 4,4'-bis(2'',3''-epoxypropyloxy)diphenylsulfone was replaced by an epoxidized novolak cresol resin (available under the trademark of Denacol EM-125, from Nagase Kasei.)

The test results are shown in Table 5.

Example 22

The same procedures as in Example 16 were carried out except that, in the preparation of the aqueous dye precursor dispersion A, 3-(N-isopentyl-N-ethylamino)-6-methyl-anilino-fluoran was replaced by 3-dibutylamino-6-methyl-7-anilino-fluoran.

The test results are shown in Table 5.

Comparative example 8

The same procedures as in Example 19 were carried out except that, in the preparation of the aqueous color-developing agent dispersion, p-benzyloxyphenyl N-(p-toluenesulfonyl)carbamate was replaced by 2,2-bis(4-hydroxyphenyl)propane, namely bisphenol A.

The test results are shown in Table 5.

Comparative Example 9

The same procedures as in Example 16 were carried out except that, in the preparation of the aqueous color-developing agent dispersion B-a, p-cumylphenyl N-(p-toluenesulfonyl)carbamate having a melting point of 120°C was replaced by (4-hydroxyphenyl)sulfone, namely bisphenol S.

The test results are shown in Table 5.

Table 5

Item Example No.	Whiteness of recording sheet	Low temperature ground color formation value	Retention (R) of colored image (%)
Example	16	82.4	0.10
	17	83.2	0.08
	18	82.7	0.07
	19	82.1	0.13
	20	83.2	0.07
	21	81.9	0.08
	22	83.7	0.07
Compara- tive Example	8	60.7	0.67
	9	70.6	0.20

Table 1 clearly shows that the new color-developing compounds of the formula (I) have a color-developing capability comparable with bisphenol A, which is a typical conventional color-developing agent, and the resultant thermosensitive colored image-forming layer exhibits a significantly higher whiteness than that of the conventional colored image-forming layer containing bisphenol A.

Table 2 clearly shows that, when the color-developing compound of the present invention is employed together with a colored image-stabilizing agent comprising an aziridiny compound, the resultant colored image exhibits a high resistance to oily or fatty substances and to a plasticizer, even immediately after the completion of the color development.

Table 3 clearly shows that the color-developing compounds of the formula (I) exhibit an excellent color-developing activity higher than that of bisphenol A, and the resultant colored image-forming layer has a superior whiteness significantly higher than that of the conventional bisphenol A - containing colored image - forming layer.

Table 4 shows that the employment of the colored image-stabilizing agent comprising an aziridiny compound, in combination with the specific color-developing compound of the present invention, is highly effective for enhancing the oil and plasticizer resistance of the resultant colored images, even immediately after the color development thereof.

Table 5 clearly indicates that, when the specific color-developing compounds of the formulae (I) and (II) of the present invention are used together with an aromatic epoxy compound, the resultant color images exhibit a superior resistance to oils and plasticizers, and the resultant colored image-forming layer exhibits a satisfactory whiteness, whereas a combination of a conventional phenolic color-developing agent with an aromatic epoxy compound usually causes the resultant colored image-forming layer to exhibit a lowered whiteness and an undesirably enhanced ground color-developing property at a relatively low temperature.

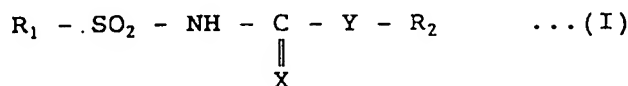
Claims

1. A thermosensitive recording material comprising:

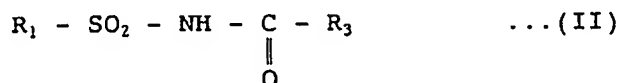
a sheet substrate, and

a thermosensitive colored image-forming layer formed on a surface of the sheet substrate and comprising a substantially colorless dye precursor, a color developing agent reactive with the dye precursor upon heating to thereby develop a color, and a binder,

said color developing agent comprising at least one aromatic sulfon(thio)amide compound selected from the group consisting of the compounds of the formulae (I) and (II):



and



in which formulae (I) and (II), X and Y respectively and independently from each other represent a member selected from the group consisting of oxygen and sulfur atoms; R₁ represents a member selected from the group consisting of unsubstituted aromatic mono- and poly- cyclic groups, and substituted phenyl groups having at least one substituent selected from the group consisting of lower alkyl groups, aryl groups and halogen atoms; R₂ represents a member selected from the group consisting of substituted alkyl groups having at least one substituent selected from the group consisting of aralkyl and aryloxy groups, unsubstituted aromatic mono- and poly-cyclic groups, and substituted aromatic mono- and poly-cyclic groups having at least one substituent selected from the group consisting of alkyl, alkenyl, aryl, aralkyl, alkyloxy, aryloxy, aralkyloxy, alkylmercapto, arylmercapto, aralkylmercapto, alkylloxycarbonyl, aryloxycarbonyl and aralkyloxycarbonyl groups and halogen atoms; and R₃ represents a member selected from the group consisting of substituted phenyl groups having at least one substituent selected from the group consisting of lower alkyl groups, aryl groups and halogen atoms, unsubstituted aromatic mono- and poly- cyclic groups and aliphatic and cycloaliphatic hydrocarbon groups having 1 to 20 carbon atoms.

2. The thermosensitive recording material as claimed in claim 1, wherein the aromatic sulfon(thio)amide compound in the color-developing agent is present in an amount of 10 to 50% based on the total weight of the thermosensitive colored image-forming layer.
3. The thermosensitive recording material as claimed in claim 1, wherein the aromatic sulfon(thio)amide compound is present in an amount of 50% to 100% based on the total weight of the color-developing agent.
4. The thermosensitive recording material as claimed in claim 1, wherein the thermosensitive colored image-forming layer further contains a colored image-stabilizing agent comprising at least one member selected from the group consisting of aromatic compounds having at least one epoxy group and organic compounds having at least one aziridiny group.
5. The thermosensitive recording material as claimed in claim 4, where the colored image-stabilizing agent is present in an amount of 1 to 30% by weight in the thermosensitive colored image-forming layer.
6. The thermosensitive recording material as claimed in claim 1, wherein the aromatic compounds having at least one epoxy group for the colored image-stabilizing agent are selected from the group consisting of 4,4'-bis(2",3"-epoxypropyloxy)diphenylsulfone, 2,2-bis[4'-(2",3"-epoxypropyloxy)phenyl]propane, 1,4-bis(2',3'-epoxypropyloxy) benzene, 4-(2"-methyl-2",3"-epoxypropyloxy)-4'-benzyloxy-diphenylsulfone, 4-(2",3"-epoxypropyloxy)-4'-(p-methyldioxy)-diphenylsulfone, epoxidized o-novolak cresol resins, 4,4'-bis(2",3"-epoxypropyloxy)diphenylmethane, 4,4'-bis(2",3"-epoxypropylamino)diphenylmethane, bis(2",3"-

epoxypropyl) 4,4'-methylene dibenzoate, 4,4'-bis(2'',3''-epoxypropyloxy)biphenyl, 4,4'-bis(2'',3''-epoxypropyloxy)-3,3',5,5'-tetramethylbiphenyl, 2,6-bis(2',3'-epoxypropyloxy)naphthalene, and bis(2,3-epoxypropyl)terephthalate.

- 5 7. The thermosensitive recording material as claimed in claim 1, wherein the organic compounds having at least one aziridiny group for the colored image-stabilizing agent are selected from the group consisting of 2,4-bis(1-aziridiny carbonylamino)toluene, bis[4-(1-aziridiny carbonylamino)phenyl]methane, bis[3-chloro-4-(1-aziridiny carbonylamino)phenyl]methane, 2,2-bis[4-(1-aziridiny carbonyloxy)phenyl]propane, and 1,4-bis(1-aziridiny carbonyl)benzene.

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 1935

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 531 139 (M.E.A. SEITZ) * column 15, line 67 - column 16, line 36; claims 4,9 * * column 18, line 29 - line 67 *	1-7	B41M5/30
A	CHIMICAL ABSTRACTS, vol. 107, no. 14, 5 October 1987, Columbus, Ohio, US; abstract no. 124649R, STANDARD REGISTER COMPANY: 'COLOUR DEVELOPER FOR PRESSURE- OR HEAT-SENSITIVE RECORDING PAPER' page 597; column 1; * abstract *	1-7	
A	EP-A-0 104 353 (HODOGAYA CHEMICAL COMPANY LIMITED) * page 3, line 18 - page 4, line 6; claim 1; table 1 *	1-7	
A	GB-A-2 062 664 (CIBA-GEIGY AG.) * page 1, line 1 - line 13; claim 1 *	1-7	
A	PATENT ABSTRACTS OF JAPAN vol. 9, no. 18 (M-353)(1741) 25 January 1985 & JP-A-59 165 678 (NIPPON KAYAKU K.K.) 18 September 1984 * abstract *	1-7	TECHNICAL FIELDS SEARCHED (Int. Cl.5) B41M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02 JUNE 1992	Examiner BACON A.J.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p>			

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